THE STATES OF IRON IN NITRIC ACID

BY JOSEPH GRANT BROWN

Two distinct states of metals with reference to their rate of dissolution have long been recognized. They have been termed the active and the passive. Iron, cobalt, tin, chromium, nickel, lead and other metals show these states definitely. Under some conditions a third state, called the semi-passive, is shown, although this state is not as definite as the others.

While a great amount of work has been done upon the subject, there is no general agreement as to what distinguishes the different states nor as to the process by which the change from one state to another takes place. Although it is probable that the cause of these states is the same in all cases, it is well known that there are a number of different conditions under which the change from one to another takes place. It would seem, therefore, that a solution of the problem can be expected only by making a detailed study of some one process.

Undoubtedly the dissolution of iron in nitric acid is one of the most complicated processes that could be selected; yet it has the advantage of a spontaneous change from one state to the other under ordinary conditions, and hence it has been chosen as the subject for such a study.

Historical

Numerous brief accounts of the action of nitric acid upon iron were published prior to 1865, but at that time Ordway[1] published a paper on "Nitrates of Iron" which gives the results of a great number of careful experiments. Work upon the action of metals on nitric acid has been done by Russell,[2] Divers,[3] Veley,[4] Armstrong and Ackworth[5] and others, but the most exhaustive study has been made by Freer and Higley.[6] Their work extended over several years and is reported in a series of papers entitled "The Action of Metals on Nitric Acid." The action of iron is given in their last paper[7] together with a summary of their work

on other metals, and some work on the electrolysis of nitric acid. The electrical conductivity of nitric acid has been measured for all concentrations by Veley and Manley.[8]

Papers dealing with the passive state of iron have been so numerous that several bibliographies have been compiled. Of these the most comprehensive is that of Heathcote.[9] A great deal of the work referred to in these bibliographies deals with the action of iron on nitric acid, but the material is scattered through a great many papers and hence it is not easy to determine just what has been done.

A paper by Young and Hogg[10] on "The Passivification of Iron by Nitric Acid" gives complete results upon the reaction velocity in acid of different density and definitely connects the passive state with certain products.

Chemical Action

A review of the chemical action of iron in nitric acid will be desirable before proceeding with a consideration of the states of iron. This will be limited to the action of pure iron in an excess of acid at room temperature, since these are the conditions under which the experimental work reported in this paper has been done.

Scheurer-Kestner[11] says that in 1.034 density acid only ferrous nitrate is formed; in 1.073 density acid both ferrous and ferric nitrate are formed; while in 1.115 density acid only ferric nitrate is formed.

Ordway found that in dilute acid, up to 1.05 density, the products of the reaction were ferrous nitrate, ammonium nitrate and a small amount of nitric oxide. In stronger acid, up to 1.20 density, he found principally ferric nitrate, small amounts of ferrous and ammonium nitrates, and a considerable amount of nitric oxide.

Freer and Higley paid no attention to the iron salts formed but made careful determinations of all the reduction products. The results of their experiments are shown in the accompanying curves (Fig. 1), in which the abscissas represent acid density and the ordinates represent the percent of equivalent

iron corresponding to the relative amount of the product formed in each case.

It must be remembered that these percents do not give the actual amounts of the products formed but only the relative amounts of each to the total products. In dilute acid the principal product is the ammonia and as the strength of the acid increases this product falls off and is not formed in acid of greater density than 1.26. Nitric oxide is also an important product of the reaction in dilute acid and it increases with the density up to about 1.28 when it begins to fall off and is not found in 1.40 acid. Small amounts of nitrogen and of nitrous oxide are formed, and these, like the nitric oxide, reach maxima
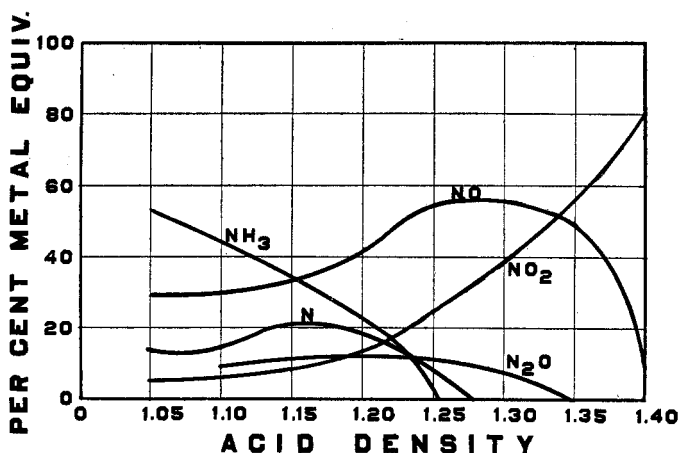

Fig. 1

and disappear as the acid becomes denser. Only a small amount of nitrogen peroxide is formed in dilute acid, but this constantly increases with the density and in concentrated acid it is the only reduction product.

The mode of action of metals was carefully considered by Freer and Higley in connection with their work. They pointed out that there are two characteristic reactions, both of which result in the formation of reduction products. The first of

these, termed the nascent hydrogen reaction, is illustrated by the action of zinc upon dilute acid and it results in the greatest possible reduction of the acid:

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

The second reaction, termed direct deoxidation, is illustrated by the action of copper upon concentrated acid, and it results in the least possible reduction of the acid:

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

The fact that both ammonium nitrate and nitrogen peroxide are obtained when iron acts upon nitric acid shows that both of these reactions are present, the nascent hydrogen reaction being specially characteristic of dilute acid and the deoxidation reaction specially characteristic of concentrated acid. Freer and Higley think that the nitric oxide is a result of the action between nitrogen peroxide and water and that the nitrogen and nitrous oxide can be accounted for by a more complete reduction of the nitrogen peroxide by the iron.

The products obtained by the electrolysis of nitric acid with platinum electrodes are similar in many respects to those obtained by the action of iron (Fig. 2).
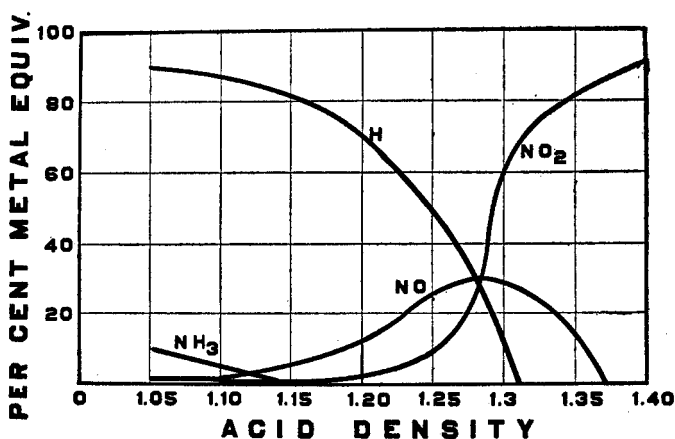

Fig. 2

Hydrogen is given off freely at the cathode in dilute acid but ceases to come off in acid slightly above 1.25 density. It begins to come off in acid of 1.30 density but suddenly ceases after a short time. Ammonia is the principal reduction product in dilute acid but ceases in 1.15 acid. It is noticeable that nitric oxide reaches a maximum and nitrogen peroxide increases rapidly in acid of 1.28 density; and that nitric oxide falls off and nitrogen peroxide becomes the only product in concentrated acid.

The reaction velocity experiments of Young and Hogg show a sudden change in the reaction velocity constant between densities of 1.25 and 1.26. Since this is the concentration which first produces the passive state, they termed it the "passive break." It is extremely significant that this density
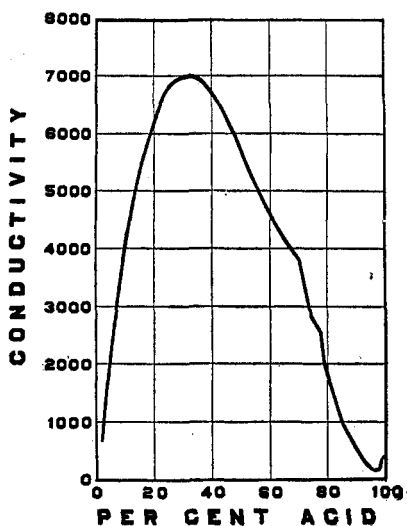

Fig. 3

corresponds closely with the density at which ammonium nitrate ceases to occur as a reduction product and hydrogen ceases to come off in electrolysis. Young and Hogg reached

the conclusion that nitrogen peroxide is the cause of the passive state but they did not feel that they could say why it should produce this state or what is the ultimate mechanism of the process.

The electrical conductivity of nitric acid at 15 degrees Centigrade was determined for all concentrations by Veley and Manley. Their curve is reproduced in Fig. 3.

The conductivity reaches a maximum in 30% acid, corresponding to a density of about 1.15, then falls off gradually to 70%, corresponding to a density of about 1.35, where it falls suddenly and becomes almost zero in 97% acid.

Experimental

It appears from the above that the action of iron on nitric acid has been studied rather fully from the standpoint of products and rate of reaction. In order to connect these results with the states of iron, it seemed desirable to make a more extensive study of the electro-chemical relations involved. Hence experimental work along this line has been undertaken and the results are given below.

In order to simplify matters as much as possible, the present work has been done with a voltaic cell. The advantages of such a cell are: that its electromotive force is a direct indicator of the state of the iron; the condition of the surrounding electrolyte may be readily observed; and practically no current needs to flow, so that polarizations due to electrolysis are eliminated.

The experiment consisted in forming the cell: $Fe_|HNO_3$ solution | concentrated HNO_3 |Pt, and measuring its electromotive force from the instant the cell was formed until the electromotive force reached a steady value, both with the iron in motion and with the iron at rest. Observations were made with a low power microscope upon the changes which took place about the iron when it was brought to rest. This was done for the following series:

TABLE I

Acid density	Grams per cc.
1.01	.0109
1.09	.155
1.12	.202
1.17	.279
1.25	.398
1.32	.507
1.37	.594
1.41	.675

A great deal of preliminary work was necessary to find the conditions under which reliable results could be obtained. This included methods of treating the iron, the form and makeup of the voltaic cell, methods of measuring the electromotive force, effects of temperature and light upon the results, and means for eliminating or controlling polarizations. The final process was as follows: "Standardization" iron wires were sand-papered, wiped with filter-paper and covered all over with a coat of paraffine. When ready for use the paraffine was scraped from a short portion and the wire was wiped with filter-paper. The cell was made up with two glass beakers connected with cotton twine, the electrodes being clamped in insulating supports.

For measuring rapidly changing electromotive forces, the cell was connected to a mica condenser which could thus be charged and then discharged through a d'Arsonval galvanometer. The capacity of the condenser was adjusted so that the galvanometer read directly in volts, 10 cm. equal to 1 volt. Contact of the iron with the electrolyte was made by means of a movable platform, carrying the cell, mounted upon a lever with a counterpoise. The time from the instant of making the cell until the breaking of the condenser circuit was measured with a stop-watch.

For measuring slowly changing electromotive forces, a high resistance and a key were placed in series with the cell

and galvanometer, the resistance being such that the readings were the same as when used ballistically. The whole arrangement is shown in the accompanying diagram (Fig. 4).
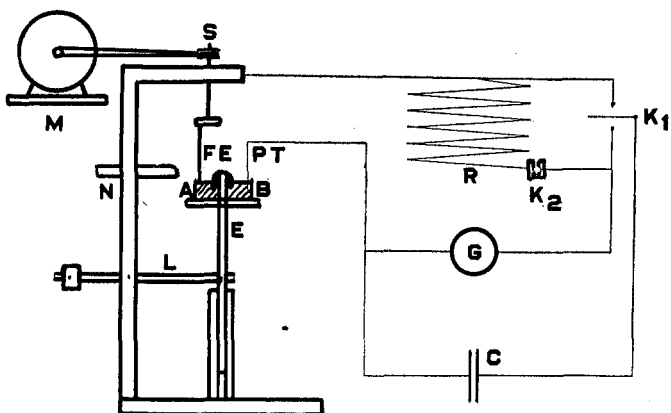

Fig. 4

A-B, Cell
C, Condenser
G, Galvanometer
R, Resistance
K_1, Charge and discharge key
K_2, Plug key
E, Movable platform

L, Lever and counterpoise
S, Spindle
M, Motor
N, Microscope
Fe, Iron
Pt, Platinum

The use of a small capacity, 2.586 M. F., and a high resistance, 832,000 ohms, practically eliminated all current, hence all changes in electromotive force are due to chemical changes independent of any electrolytic effects.

The results were obtained in two ways: first by starting with the iron at rest and then putting it in rotation after the electromotive force reached a steady value; second, by starting with the iron in rotation and then bringing it to rest after a steady electromotive force was reached. The results of the experiments in the two ways were similar, hence they will be recorded here as though they were obtained in the second way only. The following table gives the electromotive force of

the cell in volts at room temperature, 18–20 degrees, for the
different density of acid.

TABLE II

Density	Active and Semi-passive			Passive		
	Iron in motion		At rest	Either at rest or in motion		
	Starting	Steady	Steady	Max.	Min.	Final
1.01	1.25	1.25	1.54	.50	.40	Active
1.09	1.23	1.23	1.35	.45	.25	.29
1.12	1.21	1.21	1.26	.40	.20	.28
1.17	1.19	1.19	1.20	—	—	—
—	—	—	1.18	.28	.18	.26
1.25	1.18	1.18	1.06	.26	.15	.24
1.32	1.16	.99	1.01	—	—	—
—	—	—	.95	.13	.10	.25
1.37	1.16	.89	—	—	—	—
—	—	.93	Passive	.12	.08	.26
1.41	1.13	.81	—	—	—	—
—	—	.84	—	—	—	—
—	—	Passive	Passive	.08	.03	.26

Electromotive Force in Volts appears as the main spanning header.

While this table gives only the starting, steady, maximum,
minimum and final values of the electromotive force, many
intermediate values were measured so that the whole change
of electromotive force can be plotted against the time. This
has been done in a slightly conventional way in Fig. 5.

No time scale has been placed upon the plot since different
parts of the same curve are plotted on different time scales,
and the length of horizontal parts, which represent steady
states, are entirely without significance. The sloping parts
of the curves represent gradually changing electromotive force;
those represented in the upper parts of the curves take place
in a few seconds, or minutes, while those in the lower parts
require hours, days or even months.

The instant of bringing the iron to rest is marked with
an R on each curve. The vertical lines indicate instantaneous
changes in the electromotive force. In the 1.41 acid this
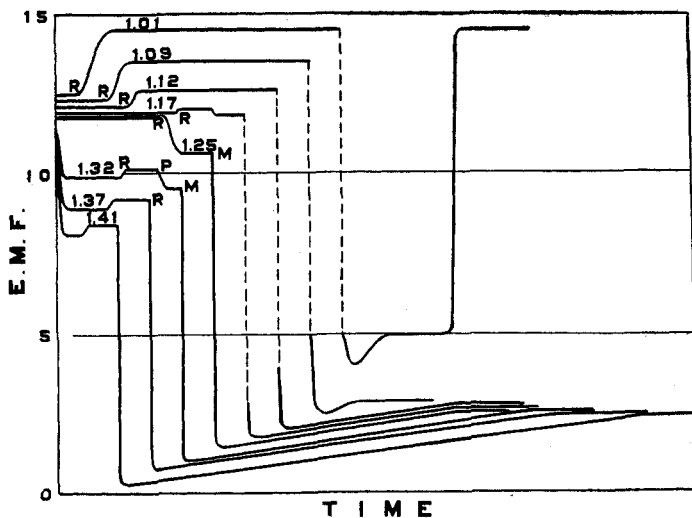instantaneous change takes place while the electrode is in

Fig. 5

motion.   In the 1.37 acid it takes place as soon as the electrode
is brought to rest.   In the 1.32 and 1.25 acids it takes place
if the iron is touched with mercury, silver, platinum or gold.
This is indicated by M on the curves.   In the more dilute
acid this sudden change in electromotive force cannot be
made to take place by touching with a metal, but if the iron
is removed, dipped in concentrated acid, and then placed
back in the dilute acid, the subsequent changes are similar
to those which take place in concentrated acid.   The broken
lines indicate that this process was followed.

It will be noticed that in dilute acid up to 1.25 density, the
electromotive force remains at the starting value as long as
the electrode is kept in motion, and that the starting values
are nearly the same in acid of all density, varying only from
1.13 volts in 1.41 density acid to 1.25 volts in 1.01 acid.   Since
the products of the chemical action are carried away by the
motion of the electrode it can be inferred that the electromotive
force results from the unpolarized electrode potential of ferrous
iron in nitric acid.   When the electrode potential was de-

termined for 1.01 acid by comparison with a calomel electrode
it was found to equal + .10 volt. The slightly smaller values
obtained in more concentrated acid are probably due to less
complete dissociation. The electrode potential of iron in
normal ferrous salts is given by Stieglitz,[12] as + .122, hence
it can be inferred that ferrous ions are formed at the instant
of making the cell in acid of all density.

No microscope observations are possible while the electrode
is in rotation, but the surface of the electrode is bright in all
dilute acid showing that in these acids the products are car-
ried away as fast as they are formed. When the electrode is
brought to rest the products of the reaction are carried away
very slowly by convection currents and by diffusion, hence
polarization takes place. As a result very marked changes
of the electromotive force occur. In acids from 1.01 to 1.12
there is a rise to a maximum steady value in each case. That
this rise is due to ferrous nitrate is shown by the fact that
when a quantity of this salt is added to the dilute acid, the
cell has an electromotive force of 1.5 volts from the start, whether
the electrode is in motion or at rest; while the addition
of ammonium nitrate or ferric nitrate does not materially
change the electromotive force of the cell. Moreover the
microscope shows the green ferrous nitrate forming about the
electrode and falling in a stream to the bottom of the cell
where it slowly dissolves in the acid.

In the 1.17 acid the rise in electromotive force is very small
and it is followed by a slight fall. The green liquid forms as
in the more dilute acid but it quickly becomes brown and loses
its color completely before reaching the bottom of the cell.
This density is evidently a critical one in the process. As
was seen above, this is the acid density at which ferrous nitrate
ceases to be found as a final product of the reaction. The value
of the electromotive force and the microscope observations
show that the same reaction is taking place as in the more
dilute solutions, but the oxidation of the ferrous nitrate to
ferric nitrate takes place so rapidly that it has practically no

effect in raising the electromotive force of the cell when the electrode is brought to rest. There is evidently a balancing of the rate at which the ferrous nitrate is formed with the rate at which it is converted into ferric nitrate, the result being that the electromotive force is practically unchanged.

In the 1.25 acid there is a considerable fall in the electromotive force when the electrode is brought to rest. This is the acid density at which ammonium nitrate ceases to be formed and the nitric oxide as a final product reaches a maximum. It is also the density at which the so-called semi-passive state of iron first appears and it marks the "passive break" in the reaction velocity constant pointed out by Young and Hogg. Microscope observations show that as soon as the electrode is brought to rest a brown liquid film forms over the surface and within this film gas bubbles are formed. The liquid which streams from the electrode is practically colorless, being slightly green.

That the same ions are given to the solution here as in the more dilute acid is shown by the fact that the electromotive force is the same when the products are carried away. The fall in the electromotive force when the electrode is brought to rest must be due to a change in the reaction and the formation of a product which produces a polarization in the opposite direction from the ferrous nitrate. When the iron is removed in this condition it is found to be covered with a slimy liquid which rapidly forms crystalline plates over the surface of the iron.

In acid of greater density than 1.25 the drop in electromotive force takes place even while the electrode is in motion. This indicates that the film clings to the surface and is not removed by the motion.

When the iron is brought to rest in the 1.32 acid there is a slight increase in the electromotive force, probably due to the presence of some ferrous nitrate. This slight rise is followed by a considerable decrease. An examination of the iron when it is first brought to rest shows the presence of the brown liquid.

and the formation of gas bubbles as in the 1.25 acid, but in this case the gas bubbles are formed at the surface and cling to the iron. A row of bubbles forms around the wire at the line where the paraffine joins the iron; a single bubble forms at the end of the wire; and more or less regular rows form over the surface of the wire. The activity is now greatest immediately under these bubbles. As a result of this local action the surface becomes pitted and the activity is confined to the bottom of the pits. During the formation of these pits the drop in electromotive force already mentioned takes place.

It is under these conditions that pulsations occur. (Marked P on the curve.) The pulsations consist of a kind of "geyser" action. The bubbles gradually increase in size and then the action suddenly stops, the bubbles being strongly repelled from the iron. The electrolyte now settles into the depressions and the action starts over again. At the instant of starting, the iron appears quite black. This action takes place simultaneously all over the surface, but at the line of separation between the iron and the paraffine the gas does not completely cease to flow. As a result of this continuous activity, the electrode is dissolved very rapidly along the line of separation and consequently is cut off long before the main body of the wire is dissolved. When such a piece is cut off it usually becomes passive over the whole surface immediately.

If the electrode is made several centimeters long only a few pulsations occur and then the whole surface becomes passive. When this happens the brown film quickly disappears and the iron has the silvery appearance characteristic of the passive state.

During the pulsating process the electromotive force drops to very low values at the instant of cessation of action and repelling of the bubbles, but no satisfactory measurements can be made since the period of cessation is so short. When the whole surface becomes passive the first electromotive force that can be measured is very small, but it continues to

decrease for some time when it reaches a minimum and then slowly increases to the final value which it maintains indefinitely.

In the 1.37 acid the process is similar to that in the 1.32 acid but no pulsations occur, the iron becoming passive as soon as it is brought to rest. In the 1.41 acid the iron becomes passive while it is kept in motion, but maintains a steady electromotive force for a short time in the semi-passive condition.

If iron which has been blued by heating in a gas flame is used as an electrode in any acid of greater density than 1.25, the electromotive force starts with the same value as when bright iron is used, but quickly goes to the low values without showing any indication whatever of an intermediate electromotive force. The presence of iron oxide apparently favors the production of the passive condition and prevents the formation of the semi-passive state. The oxide soon dissolves after the passive state is reached and the surface becomes bright.

The electrical action of the cell after the iron becomes passive is very similar in acid of all densities. Except in very dilute acid the final electromotive force is nearly the same in all cases, about .27 volt. The more concentrated the acid the smaller is the minimum value attained and the longer it takes to reach the final value.

An examination of the iron with a rather high power microscope shows that immediately after it becomes passive the surface becomes covered with very fine, transparent, needle-like crystals, and that a yellowish green liquid is formed among these crystals. No gas can be seen given off. Iron that has been passive for several weeks and has reached the final electromotive force shows no crystals and no trace of any liquid or gaseous film. The surface has the bright metallic luster of platinum.

If an electrode which has recently been made passive has the crystals rubbed off with filter-paper, and is then placed in concentrated acid, the electromotive force goes immediately

to the final value and then gradually drops to the minimum again. If an electrode which has reached the final condition is made active by touching with active iron in dilute acid and is then placed in concentrated acid, the electromotive force drops gradually to the minimum but soon returns to the final value.

These results seem to indicate that the drop in electromotive force below the final value is due to a polarization by the crystals, and that the final state is reached only after the crystals have dissolved. The chemical action which forms the crystals seems to be a last trace of activity, possibly by the iron just under the surface, after the general surface has become passive. This is indicated by the fact that the crystals seem to push out through small openings. In one case a single crystal was seen to push out fully a millimeter.

The very large, instantaneous drop in the electromotive force when the iron changes from the active to the passive state must be accompanied by a very marked change in the chemical reaction, involving a change in valence of the iron ion. It seems certain that there is a definite reaction between the passive iron and the nitric acid. Young and Hogg have shown that the rate of dissolution of passive iron is about one ten-thousandth of the rate for active iron. This means the same amount of passive iron dissolves in a week as of active iron in a minute. Pieces of passive iron wire have been kept in 1.25 acid for over a year, but all such pieces finally dissolved.

Theoretical

When these results are examined in connection with the chemical experiments enumerated above, a fairly complete notion can be obtained of the process taking place when iron acts upon nitric acid of different densities.

Iron unites with oxygen to form three oxides, one of which is commonly considered a combination of the other two. These oxides unite with water to form compounds which are amphoteric, i. e., which react with either acids or bases in the formation of salts. The oxides, together with the corre-

sponding hydroxides, are shown in the following diagram (Fig. 6), with their probable structural formulae. In order to indicate the amphoteric nature of the compounds, the ionization of the oxides has been indicated, as well as the ionization of water. The negative ion of the oxide and the positive ion of water constitute the acidic compound, while the positive ion of the oxide and the negative ion of water constitute the basic compound. Circles enclose the positive ion in every case.
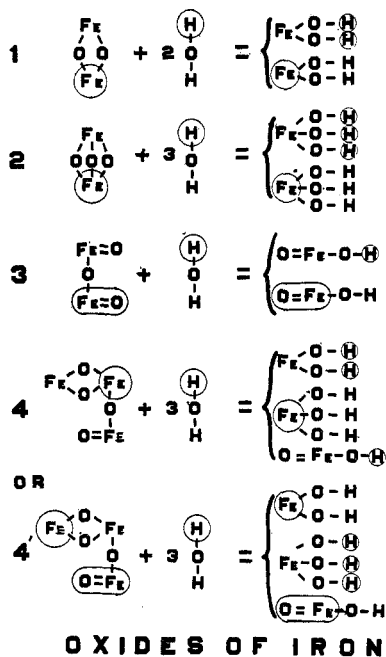

OXIDES OF IRON

Fig. 6

1. Ferrous oxide + water = ferrous hydroxide
2. Ferric oxide + water = ferric hydroxide
3. Ferric oxide + water = meta ferric hydroxide
4. Ferroso-ferric oxide + water = {
   ferrous hydroxide
   ferric hydroxide
   meta-ferric hydroxide
   }

Since these compounds are weak bases or weak acids, the ionization of the oxide must be of the same order of magnitude

as the ionization of water and therefore the numbers of each of the ions must be of the same order of magnitude. It is this condition which makes the compounds amphoteric.

Any reaction which results in the formation of one of these oxides, or hydroxides, from another involves a change in the valence of the iron. Since increased oxygen necessitates increased valence and decreased oxygen necessitates decreased valence, such changes in valence are commonly termed oxidations and reductions. The ease with which change of valence takes place and the tendency to form compounds with mixed valence are marked characteristic properties of iron.

Nitric acid is the strongest oxy-acid known. It results from the combination of nitrogen pentoxide with water, and thus stands at one end of a remarkable series of compounds of nitrogen, at the other end of which stands ammonium hydroxide. The structural formulae of some of these compounds and their ionization in combination with water are shown in Fig. 7.

In dilute aqueous solutions of nitric acid the hydrogen ion concentration is very large, hence the nitrate ion (NO_3^-) concentration must also be large. If we assume, as is usually done, that the dissociation of water is very slight, then the hydroxyl ion concentration must be very small.

When the concentration of nitric acid is increased, the hydrogen ion concentration falls off very rapidly as shown by its computation from hydrogen electrode potentials in solutions up to normal. This necessitates a corresponding decrease in the nitrate ion concentration and a considerable increase in the hydroxyl ion and nitro ion (NO_2^+) concentrations.

As a result of these changes, increased concentration of the nitric acid will ultimately result in a condition in which the order of magnitude of the numbers of each ion will be the same. When this condition is reached the acid must be considered weak and may be expected to act as an amphoteric solution.

Any reaction in the nitric acid which increases the hydrogen ion concentration furnishes the condition for reduction of the pentoxide of nitrogen to lower oxides. These oxides, when formed, may be thought of as dissociating and combining with water to form the lower compounds in the series as shown in the diagram. It is evident that in the most dilute acid such reduction may be expected to be the greatest, i. e., to ammonia, while in more concentrated acid the reduction will not proceed so far.
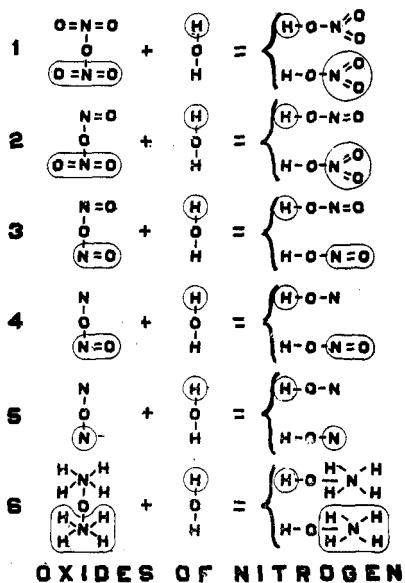

OXIDES OF NITROGEN

Fig. 7

1. Nitrogen pentoxide + water = nitric acid
2. Nitrogen peroxide + water = { nitrous acid / nitric acid
3. Nitrogen trioxide + water = nitrous acid
4. Nitric oxide + water = { hyponitrous acid / nitrous acid
5. Nitrous oxide + water = hyponitrous acid
6. Ammonium oxide + water = ammonium hydroxide

That a change such as is outlined above actually takes place in acid of increasing density, is indicated by a number of facts already mentioned. First, the conductivity, and hence the total ionization, begins to fall off in acid of 1.15 density; drops suddenly in acid of 1.35 density; and becomes extremely small in pure acid. Second, the reaction rate suddenly changes at a density of about 1.26. Third, electrolysis gives hydrogen and small amounts of nitrogen peroxide in acid below this density, but nitrogen peroxide and small amounts of hydrogen in acid above this density. Fourth, the reaction of dilute acid with iron gives only ferrous nitrate, its oxidation to ferric nitrate taking place more rapidly and more completely as the density of the acid increases. Fifth, ammonium nitrate is the principal reduction product with iron in dilute acid and its formation ceases when 1.26 acid is reached. Sixth, nitrogen peroxide is found in constantly increasing amount until it becomes the only reduction product in concentrated acid. Finally, the electromotive force of a cell with an iron anode starts with the same value in acid of all densities, but polarizations occur which constantly reduce the electromotive force as the density increases, the change from negative polarization to positive occurring in about 1.26 acid.

Assuming that double dissociation takes place as has been suggested, the action of iron on nitric acid may now be sketched in detail. Upon introducing iron into dilute acid, ferrous ions go into solution and the electrons thus liberated charge the iron negatively. If the charge is not removed a state of equilibrium will be established and the action will stop. There are two different positive ions, H^+ and NO_2^+, which may be attracted to the iron and by taking up electrons may become molecular and escape into the solution. When this occurs the charge on the iron will be reduced and the action will proceed. It is evident that hydrogen ions do not reduce the charge since no hydrogen is set free in acid of any density. Nitrogen peroxide is set free in small amount in dilute acid and constantly increases in amount as the density increases,

hence it is possible that it may reduce the charge. As will be seen below, it is quite probable that this does not happen except in concentrated acid.

There are two different negative ions with which the ferrous ions may unite, (NO_3) and (OH), hence two primary reactions are possible, thus,

(a) $Fe^{++} + 2(NO_3^-) = Fe (NO_3)_2$

(b) $Fe^{++} + 2(OH^-) = Fe (OH)_2$

Ferrous nitrate is formed in dilute acid and we know that nitrate ions are in excess, hence it is to be expected that the first reaction predominates, though there is nothing to preclude a limited amount of the second reaction. If ferrous hydroxide is formed, it undoubtedly reacts immediately with nitric acid to form ferrous nitrate, or it is oxidized as indicated below.

In order to account for the other products it will be necessary to assume varying amounts of reduction of the nitro ions by the hydrogen and ferrous ions; or, what amounts to the same thing, varying amounts of oxidation of hydrogen and ferrous ions by nitro ions.

There are three possible stages at which the oxidation of ferrous ions may take place. If ferrous nitrate has been formed and is oxidized to ferric nitrate, the process may be represented by the following equation:

$$Fe (NO_3)_2 + 2(NO_2^+) = Fe (NO_3)_3 + (NO^+)$$
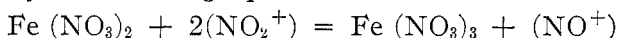
This will reduce the valence of the nitrogen from 5 to 3, and increase the valence of the iron from 2 to 3. If ferrous hydroxide has been formed and is oxidized to ferric nitrate, the reaction may be the following:

$$Fe (OH)_2 + 4(NO_2^+) = Fe (NO_3)_3 + N^+ + H_2O$$
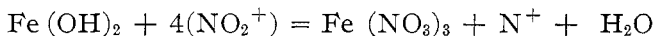
This will reduce the valence of nitrogen from 5 to 1. Finally, the oxidation may take place before the ferrous ion unites with a negative ion, in which case the nitro ion will take an electron from the ferrous ion and become molecular without a change in the valence of the nitrogen.

The reduction of the nitro ion by varying amounts of hydrogen ions is shown by the following equations:

(a) $(NO_2^+) + 2H^+ = (NO)^+ + H_2O$

(b) $(NO_2^+) + 4H^+ = N^+ + 2H_2O$

(c) $(NO_2^+) + 8H^+ = (NH_4^+) + 2H_2O$
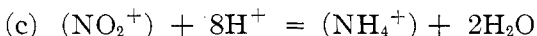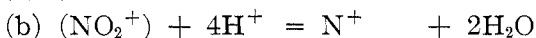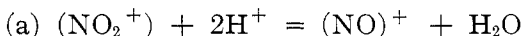
The valence of the nitrogen is thus reduced from 5 to 3, 1, and −3. The positive ions thus formed may unite with negative ions; or they may be attracted to the iron and take up electrons, thus becoming molecular. One combination which takes place is evidently the union of (NH_4^+) with (NO_3^-) to form ammonium nitrate. The N^+ and NO^+ ions are attracted to the iron, where they are set free by reducing the charge. The nitrous oxide may be accounted for by assuming that N^+ ions unite with OH^- ions to form hyponitrous acid. This acid is known to be unstable and breaks down into nitrous oxide and water.

By comparing these assumptions with the results shown in Fig. 1, it will be seen that they fully account for the variations in the relative amounts of the different products and for the order in which they disappear.

The variation in the polarization of the cell is best accounted for by a gradual substitution of some product for the ferrous nitrate. According to the assumptions just made, the most probable product is ferrous hydroxide. There is considerable evidence that ferrous hydroxide is formed in acid of intermediate density. When the electrode is removed and rubbed between the fingers it has a slimy feeling, and the red or brown color which appears is characteristic of the formation of ferric salts from ferrous hydroxide. The formation of nitrogen in the film also agrees with this assumption.

It seems probable, therefore, that the semi-passive state is associated with the gradual change from the first primary reaction, which is acidic, to the second primary reaction, which is basic.

The final point to be considered is what happens when the

iron becomes passive. It is the writer's belief that the iron ceases to form ferrous ions, but forms ferric ions instead. It has been pointed out that although nitro ions are formed in dilute acid, they will be reduced by hydrogen ions and the ions which oxidize the iron will be NO^+ and N^+. When the acid is concentrated the hydrogen ion concentration will decrease and hence the reducing action upon the nitro ions will fall off. This will result in the solution finally becoming amphoteric and the basic reaction may predominate.

It seems reasonable to suppose that under these conditions the nitro ions actually react with iron to form ferric ions, thus:
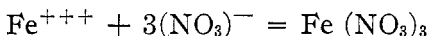
$$Fe + 3(NO_2)^+ = Fe^{+++} + 3NO_2$$
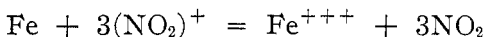
Assuming that the basic reaction exists, the principal primary reaction would be the formation of ferric hydroxide, thus:

$$Fe^{+++} + 3(OH)^- = Fe\ (OH)_3$$
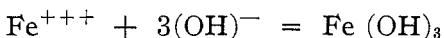
If the ferric hydroxide is dissolved in the acid the secondary reaction would be:

$$Fe\ (OH)_3 + 3HNO_3 = Fe\ (NO_3)_3 + 3H_2O$$
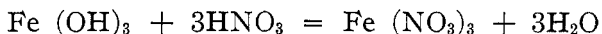
If the acidic reaction also took place, the equation would be:

$$Fe^{+++} + 3(NO_3)^- = Fe\ (NO_3)_3$$

Thus ferric nitrate and nitrogen peroxide would be the only products formed.

Nitrogen peroxide is a liquid at the temperature of the experiments and is readily absorbed by passive iron. This was shown directly by Young and Hogg. When iron which has been made passive in nitric acid is made active in the air, nitrogen peroxide is given off, as is shown by the formation of the brown fumes of nitric oxide.

The absorption of nitrogen peroxide and the existence of the passive state seem to be intimately connected and it is quite likely that the amount of oxide absorbed has much to do with the length of time that the iron remains passive when removed from the acid.

The evidence that passive iron gives off ferric ions seems quite conclusive. When the electrode of the voltaic cell be-

comes passive, the electromotive force drops instantly about one volt. Moreover, the final electromotive force is nearly the same in acid of all density, the variations being in the same direction and of the same magnitude as the variations in the starting electromotive force. Such a result as this cannot be due to a polarization, for in that case the change would be gradual and much smaller. The electrode potential of passive iron in nitric acid is —.88 volt. P. F. Hammond,[13] in his paper, "The Influence of the Metallic Ions upon the Electric Potential of a Metal Placed in the Solution," gives the electrode potential of the ferric ion as —.94 volt. This agreement indicates strongly that passive iron is ferric.

The theory that the active state of iron is ferrous and the passive state ferric is usually attributed to Finkelstein.[14] He was led to this suggestion by the change in the electrode potential of iron in mixed ferrous and ferric chloride solutions as the relative amount of the salts varied. He considered ordinary iron to be a mixture of ferrous and ferric, while passive ferric iron was considered to be a noble form of the metal produced by a process of oxidation in the passivifying liquid.

Ordinary contact electromotive force measurements place iron near tin in the Volta series, and ordinary electrolytic measurements place iron near tin in the electrode potential series. This would make it appear that ordinary iron is ferrous. Sanford[15] has pointed out, however, that the properties of iron which are determined by its cohesion would place it near platinum in the Volta series, and he has shown experimentally that when passive iron is used in contact potential experiments it is strongly electronegative.[16]

Many of the chemical properties of iron indicate that it is far more like platinum than like tin.

Hence, there is good reason for supposing that ordinary iron is essentially ferric; that it is a noble metal. In that case the reason that ordinary electrical experiments make iron appear as ferrous must be that the conditions surrounding the surface are such that only ferrous ions are formed. From

this standpoint it would be more proper to speak of active iron as "debased" than of passive iron as "ennobled."

That iron acts as divalent under ordinary conditions while it is essentially trivalent does not seem at all improbable. Valence is undoubtedly an electrical condition determined by the absence or presence of electrons in the ions formed. Iron is characterized by having three electrons which may be given up when it forms ions. Under some conditions it gives up only two of these electrons and forms divalent ions, whereas under other conditions it gives up all three electrons and forms trivalent ions. The only peculiarity is that the conditions for the first process are common, while those for the second are rare, and only occasionally, as in the case of nitric acid, the conditions for both processes exist in the same solution.

If these conclusions are correct, it would seem that they should apply to other metals which form double series of salts which readily change from one to the other. The other metals which are known to show both the active and passive states in nitric acid are chromium, cobalt, tin, nickel and lead, and these all possess this property.

It would seem also that other solutions which possess the characteristics of both acids and bases should show both states of certain metals. The action of iron has already been studied by the above methods in hydrochloric acid, sulphuric acid, chromic acid and potassium dichromate. Ordinary concentrated hydrochloric and sulphuric acids showed no tendency to form both states, while chromic acid and potassium dichromate gave results similar to nitric acid.

It is well known that iron becomes passive if made the anode of certain electrolytic cells, when a certain density of current is maintained. The necessary density of current increases as the dilution of the solution increases. It would seem that when the electrons are carried away from the iron fast enough the electrolyte may furnish the conditions which cause the formation of ferric ions when it otherwise would not. It

may be considered that the current carries the hydrogen ions to the cathode, while the hydroxyl ions are carried to the anode. This reduces the acidic character of the electrolyte about the anode and increases its basic character, with the result that the basic reaction takes place and the iron begins to form ferric ions.

Stated in simple form, the theory is that iron is essentially ferric; that it forms ferric ions in bases and weak acids where the reaction is very slow; but it forms ferrous ions in strong acids where the reaction is very rapid.

There is a possibility that iron gives off both ferrous and ferric ions in the active state. The action in nitric acid could be accounted for on this assumption quite as well as on the assumption that only ferrous ions are formed. This is a subject for further investigation.

It is believed that the principles involved in this theory are of general application. It seems probable that elements which form weak acids or weak bases possess atomic structures such that slight variations in the physical conditions will cause them to change their valence and even their sign with reference to the components of water. The loss or gain of a single electron might affect the electrical condition very greatly or very slightly depending upon the number of electrons involved and their positions in the atom.

The position of the elements in the contact potential series or electrode potential series must depend in part upon the valence and sign of the ions which are formed under the conditions used for comparison. The ordinary condition under which comparisons are made is in the presence of water at ordinary temperatures. An entirely different set of conditions might result in different positions for some of the elements. Certain elements form extremely stable compounds with water and hence slight changes in physical conditions would not be likely to change their ionization. Other elements form very unstable compounds with water and their ionization would be likely to change with slight variations in the physical

conditions. Potassium is an example of the first class while chromium is an example of the second class.

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